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CYCLOOCTATETRAENETITANIUM COMPLEXES CONTAINING TWO ACETYLENE UNITS

M.E.E. VELDMAN, H.R. VAN DER WAL, S.J. VEENSTRA and H.J. DE LIEFDE MEIJER *

*Laboratorium voor Anorganische Chemie, Rijksuniversiteit, Nijenborgh 16,
9747 AG Groningen (The Netherlands)*

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Summary

$(C_8H_8TiCl \cdot THF)_2$ reacts with acetylenes RC_2R' ($R = R' = Ph$; $R = R' =$ *p*-tolyl; $R = Ph$, $R' = Me$) and i-PrMgCl to give the binuclear complexes $(C_8H_8TiRC_2R')_2$. The IR and mass spectra and preliminary data on the crystal structure of $(C_8H_8TiPhC_2Me)_2$ indicate that one of the titanium atoms is part of a titanacyclopentadiene ring, while the other is π-bonded to this ring. Planar cyclooctatetraene rings are *octahapto* coordinated to each titanium atom. The NMR spectra of the complexes can be explained by assuming a fluxional behaviour in solution. Heating of the complexes yields the sandwich compounds $C_8H_8TiC_4R_2R'_2$.

Introduction

Van Oven et al. reported the synthesis of the sandwich complex $C_8H_8TiC_4Ph_4$ from $TiCl_3$, cyclooctatetraene and diphenylacetylene in the presence of i-PrMgBr [1]. However, another attempted synthesis of this compound, viz. reaction of $(C_8H_8TiCl \cdot THF)_2$ with diphenylacetylene and one equivalent of i-PrMgCl, yielded a red and probably dimeric compound $(C_8H_8TiPhC_2Ph)_2$, together with hexaphenylbenzene [2]. It was suggested that the trimerization to hexaphenylbenzene had proceeded stepwise, via the cyclooctatetraenetitanium complexes mentioned above or closely related compounds. Our results on the trimerization of acetylenes by titanium complexes will be reported elsewhere. In this paper we describe our studies of the compounds $(C_8H_8TiPhC_2Ph)_2$, $(C_8H_8TiMeC_2Ph)_2$ and $(C_8H_8TiToC_2To)_2$ (To = *p*-tolyl) and their thermal conversion into the corresponding sandwich complexes $C_8H_8TiC_4R_2R'_2$ (R, R' = Me, Ph, To).

Results and discussion

The complexes $(C_8H_8TiRC_2R')_2$ were prepared from $(C_8H_8TiCl \cdot THF)_2$ and i-PrMgCl with diphenylacetylene, methylphenylacetylene or di-*p*-tolylacetylene, respectively. Complex $(C_8H_8TiPhC_2Ph)_2$ (purified by repeated washing of the crude reaction product with THF at 0°C) was obtained as dark red crystals, poorly soluble in organic solvents. Complex $(C_8H_8TiMeC_2Ph)_2$ (purified by crystallization either from THF/pentane or toluene/pentane) was obtained as brown crystals containing THF or toluene in varying quantities. Complex $(C_8H_8TiToC_2To)_2$ was purified by crystallization from ether/pentane; the dark brown crystals contained one mol of ether per mol of $(C_8H_8TiToC_2To)_2$.

The complexes appeared to be stable at room temperature, but very sensitive towards oxygen and moisture. Upon heating decomposition occurred to give the cyclobutadiene sandwich complexes $C_8H_8TiC_4R_2R'_2$. Heating of $(C_8H_8TiPhC_2Ph)_2$ for 5 h at 180°C yielded $C_8H_8TiC_4Ph_4$ together with some *trans*-stilbene. The sandwich compound was isolated in about 40% yield and identified by elemental analysis, and IR and mass spectra. Similarly $(C_8H_8TiMeC_2Ph)_2$ yielded $C_8H_8C_4Me_2Ph_2$ after heating for 6 h at 260°C. Although the thermal conversion of $(C_8H_8TiToC_2To)_2$ into $C_8H_8TiC_4To_4$ was also demonstrated, the resulting sandwich complex could not be obtained pure.

The mass spectra of the complexes confirmed the presence of titanium, C_8H_8 rings and acetylene units in the molecule. The presence of ions with a high *m/e* value shows that the complexes are dimers. In the mass spectrum of $(C_8H_8TiMeC_2Ph)_2$ the molecular ion is present at *m/e* 536 (^{48}Ti). The presence of the molecular ions of the cyclobutadiene sandwich complexes $C_8H_8TiC_4R_2R_2'$ (*m/e* 508 in the spectrum of $(C_8H_8TiPhC_2Ph)_2$; *m/e* 384 in $(C_8H_8TiMeC_2Ph)_2$; *m/e* 564 in $(C_8H_8TiToC_2To)_2$ shows that some decomposition into sandwich complexes has occurred during the measurements.

The IR spectra show the η^8-C_8H_8 absorptions and the absorptions of R and R' at the expected frequencies. The peaks of THF at 1070 and 910 cm^{-1} in $(C_8H_8TiMeC_2Ph)_2 \cdot THF)_x$ and the ether absorption at 1115 cm^{-1} in $(C_8H_8TiToC_2To)_2 \cdot Et_2O$, which have frequencies closely corresponding to those of the free molecules, indicate that the ether molecules are not coordinated to the titanium atoms.

More information about the structure of the complexes was obtained from a X-ray determination. It was very difficult to get suitable crystals, and finally, measurements were made on a single crystal of $(C_8H_8TiMeC_2Ph)_2$ containing randomly distributed THF molecules. The structure could be determined by conventional methods, but no refinement was possible due to the poor quality of the data (final value of $R = 0.21$). The crystal data obtained and the most important interatomic distances are given in Table 1. The results indicate a structure as shown in Fig. 1.

The two cyclooctatetraene rings are planar and both are π-bonded to a titanium atom; titanium atom 2 is part of a titanole ring, titanium atom 1 is π-bonded to this ring. The short distance between the titanium atoms (294 pm) indicates some metal—metal bonding. The methyl groups are attached to carbons 2 and 3, the phenyl groups to carbons 1 and 4. This structure is similar to that of $(CO)_3FeC_4Ph_4Fe(CO)_3$ [3,4] and of $CpCoC_4R_4CoCp$ (R = H, Me)

TABLE I

CRYSTAL DATA FOR $(C_8H_8TiMeC_2Ph)_2$

monoclinic, space group *Cc*, *a* 1630 pm, *b* 965 pm, *c* 1744 pm, β 100.20°

standard deviations are given in brackets.

Ti(1)—Ti(2)	294 (4)				
Ti(1)—C(1)	225 (9)	Ti(2)—C(1)	221(15)	C(1)—C(2)	136(10)
Ti(1)—C(2)	228(14)	Ti(2)—C(2)	304	C(2)—C(3)	140 (9)
Ti(1)—C(3)	238 (9)	Ti(2)—C(3)	299	C(3)—C(4)	165(16)
Ti(1)—C(4)	232 (4)	Ti(2)—C(4)	198 (6)		
C(2)—Me	157(17)	C(1)—Ph	150 (9)		
C(3)—Me	139 (9)	C(4)—Ph	151(10)		

[5,6] Fig. 1.

If the structure of our complexes, as shown in Fig. 1, is retained in solution, one expects in the proton NMR spectra two signals for the cyclooctatetraene rings, one signal for the groups R attached to carbon atoms 1 and 4 and one signal for the groups R′ attached to carbon atoms 2 and 3. Although the spectra show groups R and R′ as expected, only one signal is found for the C_8H_8 rings. For instance, the ^1H NMR spectrum of $(C_8H_8TiMeC_2Ph)_2$, recorded in C_6D_6, shows one cyclooctatetraene peak (δ 6.23 ppm), one methyl signal (δ 1.77 ppm) and the phenyl protons resonating between δ 7—8 ppm. The spectrum of $(C_8H_8TiToC_2To)_2$ exhibits one signal due to the cyclooctatetraene groups (δ 6.34 ppm), two different methyl peaks of the tolyl groups (δ 1.97; 2.55 ppm), and two AB quartets of the tolyl rings (δ 6.60—7.12 and 7.35—7.93 ppm). Also the ^{13}C NMR spectrum in C_6D_6 shows only one resonance due to the cyclooctatetraene rings. An attempted assignment for the signals is given in Table 2.

The signals of the carbon atoms of the titanole ring are difficult to find. Two of these atoms resonate at δ 154.4 ppm, the signal of the other two atoms may either be hidden under the benzene peaks (δ ~128.5 ppm) or may not be present at all because of relaxation. In the latter case, the signal is expected at about δ 180 ppm.

The observed equivalence of the cyclooctatetraene rings in solution can be explained by assuming libration of the C_4R_4 group about the C(1)—C(4) axis (Fig. 3), although other possibilities cannot be excluded.

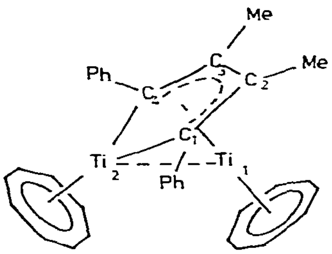


Fig. 1. Structure of $(C_8H_8TiMeC_2Ph)_2$.

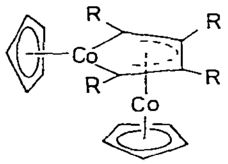
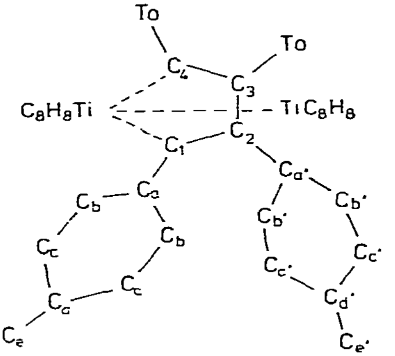


Fig. 2. Structure of $CpCoC_4R_4CoCp$.

TABLE II

TENTATIVE ASSIGNMENT OF THE CARBON-13 SPECTRUM OF $(C_8H_8TiToC_2To)_2$



Carbon:	C_8H_8	$C_{e,e'}$	$C_{a,a'}$	$C_{b,b'}$	$C_{c,c'}$	$C_{d,d'}$	C(1), C(4); C(2), C(3)
δ (ppm):	97.5	20.8	131.4	127.0	129.7	136.6	154.4
		21.2	134.3	127.5	132.2	137.4	~128.5 or ~180

The libration shown in Fig. 3 means that the titanium atoms are in turn either σ-bonded to carbon atoms 1 and 4 or π-bonded to all four. This type of fluxional behaviour has also been suggested for the cobalt compounds Cp_2Co_2-C_4R_4 (R = Me, H) [5,6] mentioned above. In the latter case libration proceeds more slowly since the ^1H NMR spectrum shows non-equivalent cyclopentadienyl rings at room temperature. At higher temperatures the two cyclopentadienyl rings become equivalent: at 90° C the resonances begin to broaden and collapse into one narrow peak at 160° C. In our compounds cooling to −85° C causes the signals to collapse but no new peaks appear. The easier libration in our compounds is probably due to the fact that the titanium atoms are larger than cobalt, so there is more space for the C_4R_4 group; moreover, neither of the two titanium atoms has an 18 electron configuration (they have 14 or 16 electrons). A transition state which requires more electrons around the metal atoms can be reached more readily in the case of titanium than in the case of the cobalt complexes, where the metal atoms have a 16 and 18 electron configuration.

The formation of cyclobutadiene complexes from metallocyclic compounds has been suggested several times but could only be proved for the conversion of

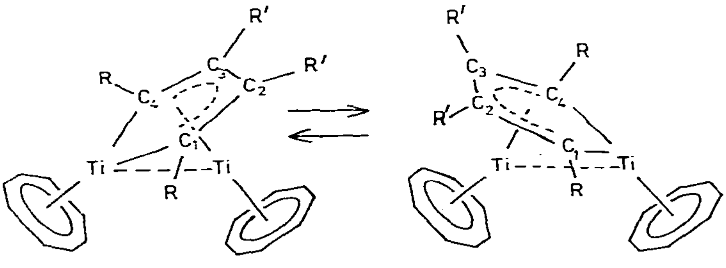


Fig. 3. Possible structure for $(C_8H_8TiRC_2R')_2$ in solution.

$CpCoPPh_3(1,4\text{-}\sigma\text{-}C_4R_4)$ into $CpCo(\pi\text{-}C_4R_4)$ [7]. The binuclear complex $((CO)_3\text{-}FeRC_2R)_2$ (R = Ph; H) could not be converted into the complexes $(CO)_3Fe\text{-}(\pi\text{-}C_4R_4)$, which are known compounds [8,9]. In our complexes this conversion occurs on heating; this may again be due to the electronic configuration of the titanium atoms; they can accept electrons more easily than the metal atoms in the iron complexes (where one Fe already has an 18-electron configuration) and this may be essential for the transformation into cyclobutadiene complexes.

Experimental

All experiments were carried out under purified nitrogen. Solvents were distilled from $LiAlH_4$ and freed from oxygen before use. Diphenylacetylene (Aldrich) was used without purification; 1-phenylpropyne was prepared from phenylethynylsodium and methyl iodide; di-*p*-tolylacetylene [10] and $(C_8H_8TiCl \cdot THF)_2$ [11] were prepared according to published procedures.

Mass spectra were run by Mr. A. Kiewiet on an AEI MS9 mass spectrometer; operating conditions: energy 70 eV, accelerating voltage 8 kV. The samples were introduced directly into the ion source using a metal probe.

^1H NMR spectra were recorded on a JEOL C-60HL instrument using TMS as an internal standard (δ = 0 ppm). The ^{13}C NMR spectra were recorded on a Varian XL100 spectrometer.

IR spectra were recorded on a Hitachi EPI-G or a JASCO IRA-2 spectrophotometer. The samples were examined as mulls between KBr windows in Voltalef 3S-oil or hexachlorobutadiene (4000—1200 cm^{-1}) and Nujol (4000—400 cm^{-1}) or in KBr discs (4000—400 cm^{-1}).

Elemental analyses were carried out at the Analytical Department of the Chemical Laboratories of this University under supervision of Mr. A.F. Hamminga.

Synthesis of $(C_8H_8TiPhC_2Ph)_2$

To a well-stirred suspension of $(C_8H_8TiCl \cdot THF)_2$ (3.69 g, 7.1 mmol) and PhC_2Ph (2.53 g, 14.2 mmol) in 60 ml of ether, 14.3 mmol of i-PrMgCl, dissolved in ether was added dropwise at room temperature. After stirring for 2 h the colour of the mixture had changed from green to red. The solvent was removed under reduced pressure and the crude reaction product was washed with THF at 0°C until the THF remained almost colourless. The residue was dark-red $(C_8H_8TiPhC_2Ph)_2$. Yield 4.05 g (6.2 mmol, 86%). Analyses: Found: C, 76.12; 76.49; H, 5.42; 5.51; Ti, 14.52; 14.53. $C_{44}H_{36}Ti_2$ calcd.: C, 80.00; H, 5.49; Ti, 14.51%. The low carbon analysis is probably due to the formation of some titanium carbide during the combustion. IR: 3040w; 1615m; 1595m; 1480m; 1440m; 1070m; 1020m; 930w; 910w; 903m; 870w; 855w; 795m; 790(sh); 768s; 760(sh); 728s; 703s; 690w; 595w; 542w; 455w cm^{-1}.

Thermal decomposition of $(C_8H_8TiPhC_2Ph)_2$

$(C_8H_8TiPhC_2Ph)_2$ (2.1 g, 3.2 mmol) was heated in a closed Schlenk tube at 180°C for 5 h. Some white material, which appeared to be *trans*-stilbene according to its IR spectrum, sublimed on the wall of the vessel. The greenblack residue was extracted with toluene (3 × 50 ml). The solution was concentrated to 50 ml and 50 ml of pentane was added. Upon cooling green $C_8H_8TiC_4Ph_4$ precipitated. Continuous extraction with hexane afforded the pure compound. Yield: 0.65 g (1.3 mmol 40%). Analysis: Ti Found 9.37, calcd. 9.42%. IR: see [1].

Synthesis of $(C_8H_8TiMeC_2Ph)_2$

The crude material was prepared from $(C_8H_8TiCl \cdot THF)_2$ (1.71 g, 3.30 mmol) and 2 equivalents of methylphenylacetylene and i-PrMgCl, as described for $(C_8H_8TiPhC_2Ph)_2$. The product was dissolved in THF (40 ml); pentane (80 ml) was added, and the solution was allowed to stand overnight at room temperature, during which the magnesium salts precipitated. The solution was then filtered and cooled to —78°C. Brown crystals separated. Yield 545 mg (0.85 mmol, 26%). Analyses: Found: C, 74.58; 74.58; H, 7.03; 7.10; Ti, 14.78; 14.95. $(C_8H_8TiMeC_2Ph)_2 \cdot 1.5$ THF ($C_{40}H_{46}OTi$) calcd.: C, 74.53; H, 6.88; Ti, 14.86%. IR: 3060w; 3040w; 1580s; 1560w; 1480s; 1440m; 1360w; 1320w; 1220s; 1177w; 1072m (THF); 1062m; 1028w; 910m (THF); 855w; 796m; 760s; 732s; 716s; 695s; 534w; 488w; 466w; 403m cm^{-1}.

Thermal decomposition of $(C_8H_8TiMeC_2Ph)_2$

Heating $(C_8H_8TiMeC_2Ph)_2$ at 260°C in a closed Schlenk tube for 6 h afforded a green product. It was recrystallized twice from hexane, but was still contaminated by some 2,3-dimethyl-1,4-diphenylbutadiene (according to its IR and UV spectra). Analysis: Found: Ti, 11.70, $C_8H_8TiMe_2Ph_2$ calcd.: Ti, 12.46%. IR: 3040w; 3000w; 2920m; 2840w; 1590s; 1530m; 1485m; 1440m; 1385m; 1365m; 1170w; 1150w; 1073w; 1020m; 908m; 792m; 768m; 748s; 733s; 692s; 612w; 642w; 476m cm^{-1}.

Synthesis of $(C_8H_8TiToC_2To)_2$

The reaction was performed as described for $(C_8H_8TiPhC_2Ph)_2$ starting from 1.14 g (2.20 mmol) of $(C_8H_8TiCl \cdot THF)_2$, and 2 equivalents of di-*p*-tolylacetylene and i-PrMgCl. To the ether solution about the same amount of pentane was added. After standing overnight (during which magnesium salts separated) the solution was filtered and cooled. Dark-brown crystals of $(C_8H_8TiToC_2To)_2 \cdot Et_2O$ (430 mg, 0.54 mmol, 25%) were obtained. Analyses: Found: C, 77.62; 78.51; H, 6.93; 6.92; Ti, 12.07; 11.97. $C_{41}H_{49}OTi_2$ calcd.: C, 78.98; H, 6.88; Ti, 12.11%. IR: 3020w; 1600w; 1550w; 1505m; 1490s; 1440(sh); 1260m; 1115s (ether); 1020w; 948m; 912m; 858m; 820m; 803s; 798s; 776w; 765m; 746m; 738m; 730s; 722s; 720s; 588m; 565w; 520m; 500m; 485m; 478m; 450m cm^{-1}.

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